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PATENT APPLICATION
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(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. 05868 USA
First Inventor or Application Identifier Mark Julian Roberts
Title HYBRID CYCLE FOR THE PRODUCTION OF LIQUEFIED
Express Mail Label No. TB827975533**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 33]
(preferred arrangement set forth below)
- Descriptive title of the invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R & D
 - Reference to Microfiche Appendix
 - Background of the invention
 - Brief Summary of the invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 9]
4. Oath or Declaration [Total Pages 3]
- a. ☒ Newly executed (original or copy)
- b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 16 completed)
- i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting
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see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

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5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
- a. ☐ Computer Readable Copy
- b. ☐ Paper Copy (identical to computer copy)
- c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement ☐ Power of
(when there is an assignee) Attorney
9. ☐ English Translation Document (if applicable)
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Statement (IDS)/PTO-1449 Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)
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13. ☐ * Small Entity ☐ Statement filed in prior application,
Statement(s) Status still proper and desired
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16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: _____
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TITLE OF THE INVENTION:

HYBRID CYCLE FOR THE PRODUCTION OF LIQUEFIED NATURAL GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

Not applicable.

BACKGROUND OF THE INVENTION

5 The production of liquefied natural gas (LNG) is achieved by cooling and

10 condensing a feed gas stream against multiple refrigerant streams provided by
recirculating refrigeration systems. Cooling of the natural gas feed is accomplished by
various cooling process cycles such as the well-known cascade cycle in which
refrigeration is provided by three different refrigerant loops. One such cascade cycle
uses methane, ethylene and propane cycles in sequence to produce refrigeration at

15 three different temperature levels. Another well-known refrigeration cycle uses a
propane pre-cooled, mixed refrigerant cycle in which a multicomponent refrigerant
mixture generates refrigeration over a selected temperature range. The mixed
refrigerant can contain hydrocarbons such as methane, ethane, propane, and other light
hydrocarbons, and also may contain nitrogen. Versions of this efficient refrigeration

20 system are used in many operating LNG plants around the world.

Another type of refrigeration process for natural gas liquefaction involves the use of a nitrogen expander cycle in which nitrogen gas is first compressed and cooled to ambient conditions with air or water cooling and then is further cooled by counter-current exchange with cold low-pressure nitrogen gas. The cooled nitrogen stream is then work
5 expanded through a turbo-expander to produce a cold low pressure stream. The cold nitrogen gas is used to cool the natural gas feed and the high pressure nitrogen stream. The work produced by the nitrogen expansion can be used to drive a nitrogen booster compressor connected to the shaft of the expander. In this process, the cold expanded nitrogen is used to liquefy the natural gas and also to cool the compressed nitrogen gas
10 in the same heat exchanger. The cooled pressurized nitrogen is further cooled in the work expansion step to provide the cold nitrogen refrigerant.

Refrigeration systems utilizing the expansion of nitrogen-containing refrigerant gas streams have been utilized for small liquefied natural gas (LNG) facilities typically used for peak shaving. Such systems are described in papers by K. Müller et al entitled
15 "Natural Gas Liquefaction by an Expansion Turbine Mixture Cycle" in *Chemical Economy & Engineering Review*, Vol. 8, No. 10 (No. 99), October 1976 and "The Liquefaction of Natural Gas in the Refrigeration Cycle with Expansion Turbine" in *Erdöl und Kohle - Erdgas - Petrochemie Brennst-Chem* Vol. 27, No. 7, 379-380 (July 1974). Another such system is described in an article entitled "SDG&E: Experience Pays Off for
20 Peak Shaving Pioneer" in *Cryogenics & Industrial Gases*, September/October 1971, pp. 25-28.

U.S. Patent 3,511,058 describes a LNG production system using a closed loop nitrogen refrigerator with a gas expander or reverse Brayton type cycle. In this process, liquid nitrogen is produced by means of a nitrogen refrigeration loop utilizing two turbo-
25 expanders. The liquid nitrogen produced is further cooled by a dense fluid expander.

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The natural gas undergoes final cooling by boiling the liquid nitrogen produced from the nitrogen liquefier. Initial cooling of the natural gas is provided by a portion of the cold gaseous nitrogen discharged from the warmer of the two expanders in order to better match cooling curves in the warm end of the heat exchanger. This process is applicable

5 to natural gas streams at sub-critical pressures since the gas is liquefied in a free-draining condenser attached to a phase separator drum.

U.S. Patent 5,768,912 (equivalent to International Patent Publication WO 95/27179) discloses a natural gas liquefaction process which uses nitrogen in a closed loop Brayton type refrigeration cycle. The feed and the high pressure nitrogen

10 can be pre-cooled using a small conventional refrigeration package employing propane, freon, or ammonia absorption cycles. This pre-cooling refrigeration system utilizes about 4% of total power consumed by the nitrogen refrigeration system. The natural gas is then liquefied and sub-cooled to -149°C using a reverse Brayton or turbo-expander cycle employing two or three expanders arranged in series relative to the cooling natural gas.

15 A mixed refrigerant system for natural gas liquefaction is described in International Patent Publication WO 96/11370 in which the mixed refrigerant is compressed, partially condensed by an external cooling fluid, and separated into liquid and vapor phases. The resulting vapor is work expanded to provide refrigeration to the cold end of the process and the liquid is sub-cooled and vaporized to provide additional refrigeration.

20 International Patent Publication WO 97/13109 discloses a discloses a natural gas liquefaction process which uses nitrogen in a closed loop reverse Brayton-type refrigeration cycle. The natural gas at supercritical pressure is cooled against the nitrogen refrigerant, expanded isentropically, and stripped in a fractionating column to remove light components.

The liquefaction of natural gas is very energy-intensive. Improved efficiency of gas liquefaction processes is highly desirable and is the prime objective of new cycles being developed in the gas liquefaction art. The objective of the present invention, as described below and defined by the claims which follow, is to improve liquefaction efficiency by providing two integrated refrigeration systems wherein one of the systems utilizes one or more vaporizing refrigerant cycles to provide refrigeration down to about -100°C and utilizes a gas expander cycle to provide refrigeration below about -100°C. Various embodiments are described for the application of this improved refrigeration system which enhance the improvements to liquefaction efficiency.

BRIEF SUMMARY OF THE INVENTION

The invention is a method for the liquefaction of a feed gas which comprises providing at least a portion of the total refrigeration required to cool and condense the feed gas by utilizing a first refrigeration system which comprises at least one recirculating refrigeration circuit, wherein the first refrigeration system utilizes two or more refrigerant components and provides refrigeration in a first temperature range; and a second refrigeration system which provides refrigeration in a second temperature range by work expanding a pressurized gaseous refrigerant stream.

The lowest temperature in the second temperature range preferably is less than the lowest temperature in the first temperature range. Typically, at least 5% of the total refrigeration power required to liquefy the feed gas is consumed by the first refrigeration system. Under many operating conditions, at least 10% of the total refrigeration power required to liquefy the feed gas can be consumed by the first recirculating refrigeration system. Preferably, the feed gas is natural gas.

The refrigerant in the first recirculating refrigeration circuit can comprise two or more components selected from the group consisting of nitrogen, hydrocarbons containing one or more carbon atoms, and halocarbons containing one or more carbon atoms. The method refrigerant in the second recirculating refrigeration circuit can
5 comprise nitrogen.

At least a portion of the first temperature range typically is between about -40°C and about -100°C, and at least a portion of the first temperature range can be between about -60°C and about -100°C. At least a portion of the second temperature range can be below about -100°C.

10 In one embodiment of the invention, the first recirculating refrigeration system is operated by

- (1) compressing a first gaseous refrigerant;
- (2) cooling and at least partially condensing the resulting compressed refrigerant;
- (3) reducing the pressure of the resulting at least partially condensed
15 compressed refrigerant;
- (4) vaporizing the resulting reduced-pressure refrigerant to provide refrigeration in the first temperature range and yield a vaporized refrigerant; and
- (5) recirculating the vaporized refrigerant to provide the first gaseous refrigerant of (1).

20 At least a portion of the cooling of the resulting compressed refrigerant in (2) can be provided by indirect heat exchange with vaporizing reduced-pressure refrigerant in (4). At least a portion of the cooling in (2) can be provided by indirect heat exchange with one or more additional vaporizing refrigerant streams provided by a third recirculating refrigeration circuit. The third recirculating refrigeration circuit typically

utilizes a single component refrigerant. The third recirculating refrigeration circuit can utilize a mixed refrigerant comprising two or more components.

The second recirculating refrigeration system can be operated by

(1) compressing a second gaseous refrigerant to provide the pressurized gaseous refrigerant in (b);

(2) cooling the pressurized gaseous refrigerant to yield a cooled gaseous refrigerant;

(3) work expanding the cooled gaseous refrigerant to provide the cold refrigerant in (b);

(4) warming the cold refrigerant to provide refrigeration in the second temperature range; and

(5) recirculating the resulting warmed refrigerant to provide the second gaseous refrigerant of (1).

At least a portion of the cooling in (2) can be provided by indirect heat exchange by warming the cold refrigerant stream in (4). Also, at least a portion of the cooling in (2) can be provided by indirect heat exchange with the vaporizing refrigerant of (a). At least a portion of the cooling in (2) can be provided by indirect heat exchange with one or more additional vaporizing refrigerants provided by a third recirculating refrigeration circuit, which can utilize a single component refrigerant. Alternatively, the third recirculating refrigeration circuit can utilize a mixed refrigerant which comprises two or more components.

The first recirculating refrigeration circuit and the second recirculating refrigeration circuit can provide, in a single heat exchanger, a portion of the total refrigeration required to liquefy the feed gas.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

Fig. 1 is a schematic flow diagram of a preferred embodiment of the present invention.

- 5 Fig. 2 is a schematic flow diagram of another embodiment of the present invention which utilizes an alternative method for pre-cooling the recirculating refrigerant in the gas expander refrigeration cycle.

- 10 Fig. 3 is a schematic flow diagram of another embodiment of the present invention which utilizes product flash gas as the refrigerant in the gas expander refrigeration cycle.

Fig. 4 is a schematic flow diagram of another embodiment of the present invention which utilizes an additional refrigeration system to pre-cool the feed gas, the compressed refrigerant in the vapor recompression refrigeration cycle, and the compressed refrigerant in the gas expander refrigeration cycle.

- 15 Fig. 5 is a schematic flow diagram of another embodiment of the present invention which utilizes an additional liquid mixed refrigerant stream in the vapor recompression refrigeration cycle.

- 20 Fig. 6 is a schematic flow diagram of another embodiment of the present invention in which heat exchange among the feed gas and two refrigeration systems is consolidated into a minimum number of heat exchange zones.

Fig. 7 is a schematic flow diagram of another embodiment of the present invention which utilizes an additional vapor recompression refrigeration system.

Fig. 8 is a schematic flow diagram of another embodiment of the present invention which utilizes a cascade refrigeration cycle to precool the feed gas.

Fig. 9 is a schematic flow diagram of another embodiment of the present invention which utilizes expander work to provide a portion of the compression work in the gas expander refrigeration cycle.

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DETAILED DESCRIPTION OF THE INVENTION

Most LNG production plants today utilize refrigeration produced by compressing a gas to a high pressure, liquefying the gas against a cooling source, expanding the resulting liquid to a low pressure, and vaporizing the resulting liquid to provide the refrigeration. Vaporized refrigerant is recompressed and utilized again in the recirculating refrigeration circuit. This type of refrigeration process can utilize a multi-component mixed refrigerant or a cascaded single component refrigerant cycle for cooling, and is defined generically herein as a vaporizing refrigerant cycle or as a vapor recompression cycle. This type of cycle is very efficient at providing cooling at near ambient temperatures. In this case, refrigerant fluids are available which will condense at a pressure well below the refrigerant critical pressure while rejecting heat to an ambient temperature heat sink, and will also boil at a pressure above atmospheric while absorbing heat from the refrigeration load.

As the required refrigeration temperature decreases in a single component vapor compression refrigeration system, a particular refrigerant which boils above atmospheric pressure at a temperature low enough to provide the required refrigeration will be too volatile to condense against an ambient temperature heat sink because the refrigerant critical temperature is below ambient temperature. In this situation, cascade cycles can be employed. For example, a two-fluid cascade can be utilized in which a heavier fluid provides the warmer refrigeration while a lighter fluid provides the colder refrigeration. Rather than rejecting heat to an ambient temperature, however, the light fluid rejects

cases, however, the working fluid can undergo a small degree of phase change during work expansion.

The gas expander cycle efficiently provides refrigeration to fluids which are also cooling over a temperature range, and is particularly useful in providing for very low temperature refrigeration such as that required in producing liquid nitrogen and hydrogen.

A disadvantage of the gas expander refrigeration cycle, however, is that it is relatively inefficient at providing warm refrigeration. The net work required for a gas expander cycle refrigerator is equal to the difference between the compressor work and the expander work, while the work for a cascade or single component refrigeration cycle is simply the compressor work. In the gas expander cycle, expansion work can easily be 50% or more of the compressor work when providing warm refrigeration. The problem with the gas expander cycle in providing warm refrigeration is that any inefficiency in the compressor system is multiplied.

The objective of the present invention is to exploit the benefits of the gas expander cycle in providing cold refrigeration while utilizing the benefits of pure or multi-component vapor recompression refrigeration cycles in providing warm refrigeration, and applying this combination of refrigeration cycles to gas liquefaction. This combination refrigeration cycle is particularly useful in the liquefaction of natural gas.

According to the invention, mixed component, pure component, and/or cascaded vapor recompression refrigeration systems are used to provide a portion of the refrigeration needed for gas liquefaction at temperatures below about -40°C and down to about -100°C . The residual refrigeration in the coldest temperature range below about -100°C is provided by work expansion of a refrigerant gas. The recirculation circuit of

the refrigerant gas stream used for work expansion is physically independent from but thermally integrated with the recirculation circuit or circuits of the pure or mixed component vapor recompression cycle or cycles. More than 5% and usually more than 10% of the total refrigeration power required for liquefaction of the feed gas can be consumed by the pure or mixed component vapor recompression cycle or cycles. The invention can be implemented in the design of a new liquefaction plant or can be utilized as a retrofit or expansion of an existing plant by adding the gas expander cooling circuit to the existing plant refrigeration system.

The pure or mixed component vapor recompression working fluid or fluids generally comprise one or more components chosen from nitrogen, hydrocarbons having one or more carbon atoms, and halocarbons having one or more carbon atoms. Typical hydrocarbon refrigerants include methane, ethane, propane, i-butane, butane, and i-pentane. Representative halocarbon refrigerants include R22, R23, R32, R134a, and R410a. The gas stream to be work expanded in the gas expander cycle can be a pure component or a mixture of components; examples include a pure nitrogen stream or a mixture of nitrogen with other gases such as methane.

The method of providing refrigeration using a mixed component circuit includes compressing a mixed component stream and cooling the compressed stream using an external cooling fluid such as air, cooling water, or another process stream. A portion of the compressed mixed refrigerant stream is liquefied after external cooling. At least a portion of the compressed and cooled mixed refrigerant stream is further cooled in a heat exchanger and then reduced in pressure and vaporized by heat exchange against the gas stream being liquefied. The evaporated and warmed mixed refrigerant steam is then recirculated and compressed as described above.

The method of providing refrigeration using a pure component circuit consists of compressing a pure component stream and cooling it using an external cooling fluid, such as air, cooling water, another pure component stream. A portion of the refrigerant stream is liquefied after external cooling. At least a portion of the compressed and

5 liquefied refrigerant is then reduced in pressure and vaporized by heat exchange against the gas stream being liquefied or against another refrigerant stream being cooled. The resulting vaporized refrigerant steam is then compressed and recirculated as described above.

According to the invention, the pure or mixed component vapor recompression

10 cycle or cycles preferably provide refrigeration to temperature levels below about -40°C , preferably below about -60°C , and down to about -100°C , but do not provide the total refrigeration needed for liquefying the feed gas. These cycles typically may consume more than 5%, and usually more than 10%, of the total refrigeration power requirement for liquefaction of the feed gas. In the liquefaction of natural gas, pure or mixed

15 component vapor recompression cycle or cycles typically can consume greater than 30% of the total power requirement required to liquefy the feed gas. In this application, the natural gas preferred is cooled to temperatures well below -40°C , and preferably below -60°C , by the pure or mixed component vapor recompression cycle or cycles.

The method of providing refrigeration in the gas expander cycle includes

20 compressing a gas stream, cooling the compressed gas stream using an external cooling fluid, further cooling at least a portion of the cooled compressed gas stream, expanding at least a portion of the further cooled stream in an expander to produce work, warming the expanded stream by heat exchange against the stream to be liquefied, and recirculating the warmed gas stream for further compression. This cycle

provides refrigeration at temperature levels below the temperature levels of the refrigeration provided by the pure or mixed refrigerant vapor recompression cycle.

In a preferred mode, the pure or mixed component vapor recompression cycle or cycles provide a portion of the cooling to the compressed gas stream prior to its

5 expansion in an expander. In an alternative mode, the gas stream may be expanded in more than one expander. Any known expander arrangement to liquefy a gas stream may be used. The invention may utilize any of a wide variety of heat exchange devices in the refrigeration circuits including plate-fin, wound coil, and shell and tube type heat exchangers, or combinations thereof, depending on the specific application. The
10 invention is independent of the number and arrangement of the heat exchangers utilized in the claimed process.

A preferred embodiment of the invention illustrated in Fig. 1. The process can be used to liquefy any feed gas stream, and preferably is used to liquefy natural gas as described below to illustrate the process. Natural gas is first cleaned and dried in
15 pretreatment section 172 for the removal of acid gases such as CO₂ and H₂S along with other contaminants such as mercury. Pre-treated gas stream 100 enters heat exchanger 106, is cooled to a typical intermediate temperature of approximately -30°C, and cooled stream 102 flows into scrub column 108. The cooling in heat exchanger 106 is effected by the warming of mixed refrigerant stream 125 in the interior 109 of heat exchanger
20 106. The mixed refrigerant typically contains one or more hydrocarbons selected from methane, ethane, propane, i-butane, butane, and possibly i-pentane. Additionally, the refrigerant may contain other components such as nitrogen. In scrub column 108, the heavier components of the natural gas feed, for example pentane and heavier components, are removed. In the present examples the scrub column is shown with

only a stripping section. In other instances a rectifying section with a condenser can be employed for removal of heavy contaminants such as benzene to very low levels. When very low levels of heavy components are required in the final LNG product, any suitable modification to scrub column 110 can be made. For example, a heavier component
5 such as butane may be used as the wash liquid.

Bottoms product 110 of the scrub column then enters fractionation section 112 where the heavy components are recovered as stream 114. The propane and lighter components in stream 118 pass through heat exchanger 106, where the stream is cooled to about -30°C , and recombined with the overhead product of the scrub column
10 to form purified feed stream 120. Stream 120 is then further cooled in heat exchanger 122 to a typical temperature of about -100°C by warming mixed refrigerant stream 124. The resulting cooled stream 126 is then further cooled to a temperature of about -166°C in heat exchanger 128. Refrigeration for cooling in heat exchanger 128 is provided by cold refrigerant fluid stream 130 from turbo-expander 166. This fluid, preferably
15 nitrogen, is predominately vapor containing less than 20% liquid and is at a typical pressure of about 11 bara (all pressures herein are absolute pressures) and a typical temperature of about -168°C . Further cooled stream 132 can be flashed adiabatically to a pressure of about 1.05 bara across throttling valve 134. Alternatively, pressure of further cooled stream 132 could be reduced across a work expander. The liquefied gas
20 then flows into separator or storage tank 136 and the final LNG product is withdrawn as stream 142. In some cases, depending on the natural gas composition and the temperature exiting heat exchanger 128, a significant quantity of light gas is evolved as stream 138 after the flash across valve 134. This gas can be warmed in heat

exchangers 128 and 150 and compressed to a pressure sufficient for use as fuel gas in the LNG facility.

Refrigeration to cool the natural gas from ambient temperature to a temperature of about -100°C is provided by a multi-component refrigeration loop as mentioned above.

- 5 Stream 146 is the high pressure mixed refrigerant which enters heat exchanger 106 at ambient temperature and a typical pressure of about 38 bara. The refrigerant is cooled to a temperature of about -100°C in heat exchangers 106 and 122, exiting as stream 148. Stream 148 is divided into two portions in this embodiment. A smaller portion, typically about 4%, is reduced in pressure adiabatically to about 10 bara and is
- 10 introduced as stream 149 into heat exchanger 150 to provide supplemental refrigeration as described below. The major portion of the refrigerant as stream 124 is also reduced in pressure adiabatically to a typical pressure of about 10 bara and is introduced to the cold end of heat exchanger 106. The refrigerant flows downward and vaporizes in interior 109 of heat exchanger 106 and leaves at slightly below ambient temperature as
- 15 stream 152. Stream 152 is then re-combined with minor stream 154 which was vaporized and warmed to near ambient temperature in heat exchanger 150. The combined low pressure stream 156 is then compressed in multi-stage intercooled compressor 158 back to the final pressure of about 38 bara. Liquid can be formed in the intercooler of the compressor, and this liquid is separated and recombined with the main
- 20 stream 160 exiting final stage of compression. The combined stream is then cooled back to ambient temperature to yield stream 146.

Final cooling of the natural gas from about -100°C to about -166°C is accomplished using a gas expander cycle employing nitrogen as the working fluid. High pressure nitrogen stream 162 enters heat exchanger 150 typically at ambient

temperature and a pressure of about 67 bara, and is then cooled to a temperature of about -100°C in heat exchanger 150. Cooled vapor stream 164 is substantially isentropically work expanded in turbo-expander 132, typically exiting at a pressure of about 11 bara and a temperature of about -168°C. Ideally the exit pressure is at or slightly below the dewpoint pressure of the nitrogen at a temperature cold enough to effect the cooling of the LNG to the desired temperature. Expanded nitrogen stream 130 is then warmed to near ambient temperature in heat exchangers 128 and 150. Supplemental refrigeration is provided to heat exchanger 150 by a small stream 149 of the mixed refrigerant, as described earlier, and this is done to reduce the irreversibility in the process by causing the cooling curves heat exchanger 150 to be more closely aligned. From heat exchanger 150, warmed low pressure nitrogen stream 170 is compressed in multistage compressor 168 back to a high pressure of about 67 bara.

As mentioned above, this gas expander cycle can be implemented as a retrofit or expansion of an existing mixed refrigerant LNG plant.

An alternative embodiment of the invention is illustrated in Fig. 2. Instead of the wound coil heat exchangers 106 and 128 shown in Fig. 1, this alternative utilizes plate and fin heat exchangers 206, 222, and 228 along with plate and fin heat exchanger 250. In this embodiment, the irreversibility in the warm nitrogen heat exchanger 250 is reduced by decreasing the flow of the cooling streams rather than by increasing the flow of warming streams. In either case the effect is similar and the cooling curves heat exchanger 250 become more closely aligned. In the embodiment of Fig. 2, a small portion of the warm high pressure nitrogen as stream 262 is cooled in heat exchangers 206 and 222 to a temperature of about -100°C, exiting as stream 202. Stream 202 is

then re-combined with the main high pressure nitrogen flow and expanded in work expander 232.

Fig. 3 illustrates another alternate embodiment of the invention. In this embodiment, the working fluid for the gas expander refrigeration loop is a hydrocarbon-nitrogen mixture from the light vapor stream 300 evolved by flashing the liquefied gas from heat exchanger 128 across valve 134. This vapor is then combined with the fluid exiting turbo-expander 132, warmed in heat exchangers 128 and 150, and compressed in compressor 368. The gas exiting compressor 368 is then cooled in heat exchanger 308. The bulk of the gas exiting 308 is passed into heat exchanger 150 and small portion 304, equal in flow to the flow of flash gas stream 300, is withdrawn from the circuit for as fuel gas for the LNG facility. In this embodiment, the functions of fuel gas compressor 140 and recycle compressor 168 of Fig. 1 are combined in compressor 368. It is also possible to withdraw stream 304 from an interstage location of recycle compressor 368.

An alternate embodiment is illustrated in Fig. 4 in which another refrigerant (for example propane) is used to pre-cool the feed, nitrogen, and mixed refrigerant streams in heat exchangers 402, 401, and 400 respectively before introduction into heat exchangers 106 and 150. In this embodiment, three levels of pre-cooling are used in heat exchangers 402, 401, and 400, although any number of levels can be used as required. In this case, returning refrigerant fluids 156 and 170 are compressed cold, at an inlet temperature slightly below that provided by the pre-cooling refrigerant. This arrangement could be implemented as a retrofit or expansion of an existing propane pre-cooled mixed refrigerant LNG plant.

Fig. 5 shows another embodiment of the invention in which high pressure mixed refrigerant stream 146 is separated into liquid and vapor sub-streams 500 and 501.

Vapor stream 501 is cooled to about -100°C , substantially liquefied, reduced to a low pressure of about 3 bara, and used as stream 503 to provide refrigeration. Liquid stream 500 is cooled to about -30°C , is reduced to an intermediate pressure of about 9 bara, and used as stream 502 to provide refrigeration. A minor portion of cooled vapor stream 505 is used as stream 504 to provide supplemental refrigeration to heat exchangers 150 as earlier described.

The two vaporized low pressure mixed refrigerant return streams are combined to form stream 506, which is then compressed cold at a temperature of about -30°C to an intermediate pressure of about 9 bara and combined with vaporized intermediate pressure stream 507. The resulting mixture is then further compressed to a final pressure of about 50 bara. In this embodiment, liquid is formed in the intercooler of the compressor, and this liquid is recombined with the main flow 160 exiting the final compression stage.

Optionally, compressed nitrogen stream 510 could be cooled before entering heat exchanger 150 by utilizing subcooled refrigerant liquid stream 511 (not shown). A portion of stream 511 could be reduced in pressure and vaporized to cool stream 510 by indirect heat exchange, and the resulting vapor would be returned to the refrigerant compressor. Alternatively, stream 510 could be cooled with other process streams in the heat exchanger cooled by vaporizing refrigerant stream 502.

Another embodiment is shown in Fig. 6 in which heat exchangers 122, 106 and 150 of Fig. 1 are combined functionally into heat exchangers 600 and 601 to yield an equipment simplification. Note that a balancing stream such as stream 168 of Fig. 1 is no longer required. In this embodiment, the vaporizing mixed refrigerant circuit and the gas expander refrigeration circuit provide in heat exchanger 601 a portion of the total

refrigeration required to liquefy the feed gas. These two refrigeration circuits also provide in heat exchanger 600 another portion of the total refrigeration required to liquefy the feed gas. The remainder of the total refrigeration required to liquefy the feed gas is provided in heat exchanger 128.

5 Fig. 7 presents an embodiment of the invention in which two separate mixed refrigerant loops are employed before final cooling by the gas expander refrigeration loop. The first refrigeration loop employing compressor 701 and pressure reduction device 703 provides primary cooling to a temperature of about -30°C. A second refrigeration loop employing compressor 702 and expansion devices 704 and 705 is
10 used to provide further cooling to a temperature of about -100°C. This arrangement could be implemented as a retrofit or expansion of an existing dual mixed refrigerant LNG plant.

Fig. 8 presents an embodiment of the invention in which a two-fluid cascade cycle is used to provide precooling prior to final cooling by the gas expander refrigeration
15 cycle.

Fig. 9 illustrates the use of expander 800 to drive the final compressor stage of the compressor for the gas expander refrigeration circuit. Alternatively, work generated by expander 800 could be used to compress other process streams. For example, a portion or all of this work could be used to compress the feed gas in line 900. In another
20 option, a portion or all of the work from expander 800 could be used for a portion of the work required by mixed refrigerant compressor 958.

The invention described above in the embodiments illustrated by Figs. 1-9 can utilize any of a wide variety of heat exchange devices in the refrigeration circuits including wound coil, plate-fin, shell and tube, and kettle type heat exchangers.

Combinations of these types of heat exchangers can be used depending upon specific applications. For example in Fig. 2, all four heat exchangers 106, 122, 128, and 150 can be wound coil exchangers. Alternatively, heat exchangers 106, 122, 128 can be wound coil exchangers and heat exchanger 150 can be a plate and fin type exchanger as
5 utilized in Fig. 1.

In the preferred embodiment of the invention, the majority of the refrigeration in the temperature range of about -40°C to about -100°C is provided by indirect heat exchange with at least one vaporizing refrigerant in a recirculating refrigeration circuit. Some of the refrigeration in this temperature range also can be provided by the work
10 expansion of a pressurized gaseous refrigerant.

EXAMPLE

Referring to Fig. 1, natural gas is cleaned and dried in pretreatment section 172 for the removal of acid gases such as CO₂ and H₂S along with other contaminants such
15 as mercury. Pretreated feed gas 100 has a flow rate of 24,431 kg-mole/hr, a pressure of 66.5 bara, and a temperature of 32°C. The molar composition of the stream is as follows:

Table 1
Feed Gas Composition

Component	Mole Fraction
Nitrogen	0.009
Methane	0.9378
Ethane	0.031
Propane	0.013
i-Butane	0.003
Butane	0.004
i-Pentane	0.0008
Pentane	0.0005
Hexane	0.001

Vapor stream 501 is cooled to about -100°C , substantially liquefied, reduced to a low pressure of about 3 bara, and used as stream 503 to provide refrigeration. Liquid stream 500 is cooled to about -30°C , is reduced to an intermediate pressure of about 9 bara, and used as stream 502 to provide refrigeration. A minor portion of cooled vapor stream 505 is used as stream 504 to provide supplemental refrigeration to heat exchangers 150 as earlier described.

The two vaporized low pressure mixed refrigerant return streams are combined to form stream 506, which is then compressed cold at a temperature of about -30°C to an intermediate pressure of about 9 bara and combined with vaporized intermediate pressure stream 507. The resulting mixture is then further compressed to a final pressure of about 50 bara. In this embodiment, liquid is formed in the intercooler of the compressor, and this liquid is recombined with the main flow 160 exiting the final compression stage.

Optionally, compressed nitrogen stream 510 could be cooled before entering heat exchanger 150 by utilizing subcooled refrigerant liquid stream 511 (not shown). A portion of stream 511 could be reduced in pressure and vaporized to cool stream 510 by indirect heat exchange, and the resulting vapor would be returned to the refrigerant compressor. Alternatively, stream 510 could be cooled with other process streams in the heat exchanger cooled by vaporizing refrigerant stream 502.

Another embodiment is shown in Fig. 6 in which heat exchangers 122, 106 and 150 of Fig. 1 are combined functionally into heat exchangers 600 and 601 to yield an equipment simplification. Note that a balancing stream such as stream 168 of Fig. 1 is no longer required. In this embodiment, the vaporizing mixed refrigerant circuit and the gas expander refrigeration circuit provide in heat exchanger 601 a portion of the total

refrigeration required to liquefy the feed gas. These two refrigeration circuits also provide in heat exchanger 600 another portion of the total refrigeration required to liquefy the feed gas. The remainder of the total refrigeration required to liquefy the feed gas is provided in heat exchanger 128.

5 Fig. 7 presents an embodiment of the invention in which two separate mixed refrigerant loops are employed before final cooling by the gas expander refrigeration loop. The first refrigeration loop employing compressor 701 and pressure reduction device 703 provides primary cooling to a temperature of about -30°C. A second refrigeration loop employing compressor 702 and expansion devices 704 and 705 is
10 used to provide further cooling to a temperature of about -100°C. This arrangement could be implemented as a retrofit or expansion of an existing dual mixed refrigerant LNG plant.

Fig. 8 presents an embodiment of the invention in which a two-fluid cascade cycle is used to provide precooling prior to final cooling by the gas expander refrigeration
15 cycle.

Fig. 9 illustrates the use of expander 800 to drive the final compressor stage of the compressor for the gas expander refrigeration circuit. Alternatively, work generated by expander 800 could be used to compress other process streams. For example, a portion or all of this work could be used to compress the feed gas in line 900. In another
20 option, a portion or all of the work from expander 800 could be used for a portion of the work required by mixed refrigerant compressor 958.

The invention described above in the embodiments illustrated by Figs. 1-9 can utilize any of a wide variety of heat exchange devices in the refrigeration circuits including wound coil, plate-fin, shell and tube, and kettle type heat exchangers.

Combinations of these types of heat exchangers can be used depending upon specific applications. For example in Fig. 2, all four heat exchangers 106, 122, 128, and 150 can be wound coil exchangers. Alternatively, heat exchangers 106, 122, 128 can be wound coil exchangers and heat exchanger 150 can be a plate and fin type exchanger as

5 utilized in Fig. 1.

In the preferred embodiment of the invention, the majority of the refrigeration in the temperature range of about -40°C to about -100°C is provided by indirect heat exchange with at least one vaporizing refrigerant in a recirculating refrigeration circuit. Some of the refrigeration in this temperature range also can be provided by the work

10 expansion of a pressurized gaseous refrigerant.

EXAMPLE

Referring to Fig. 1, natural gas is cleaned and dried in pretreatment section 172 for the removal of acid gases such as CO₂ and H₂S along with other contaminants such as mercury. Pretreated feed gas 100 has a flow rate of 24,431 kg-mole/hr, a pressure of

15 66.5 bara, and a temperature of 32°C. The molar composition of the stream is as follows:

Table 1
Feed Gas Composition

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Nitrogen	0.009
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Ethane	0.031
Propane	0.013
i-Butane	0.003
Butane	0.004
i-Pentane	0.0008
Pentane	0.0005
Hexane	0.001
Heptane	0.0006

Pre-treated gas 100 enter first heat exchanger 106 and is cooled to a temperature of -31°C before entering scrub column 108 as stream 102. The cooling is effected by the warming of mixed refrigerant stream 109, which has a flow of 554,425 kg-mole/hr and the following composition:

Table 2

Mixed Refrigerant Composition

Component	Mole Fraction
Nitrogen	0.014
Methane	0.343
Ethane	0.395
Propane	0.006
i-Butane	0.090
Butane	0.151

In scrub column 108, pentane and heavier components of the feed are removed.

Bottoms product 110 of the scrub column enters fractionation section 112 where the heavy components are recovered as stream 114 and the propane and lighter components in stream 118 are recycled to heat exchanger 106, cooled to -31°C, and recombined with the overhead product of the scrub column to form stream 120. The flow rate of stream 120 is 24,339 kg-mole/hr.

Stream 120 is further cooled in heat exchanger 122 to a temperature of -102.4°C by warming mixed refrigerant stream 124 which enters heat exchanger 122 at a temperature of -104.0°C. The resulting stream 128 is then further cooled to a temperature of -165.7°C in heat exchanger 128. Refrigeration for cooling in heat

exchanger 128 is provided by pure nitrogen stream 130 exiting turbo-expander 166 at -168.0°C with a liquid fraction of 2.0%. The resulting LNG stream 132 is then flashed adiabatically to its bubble point pressure of 1.05 bara across valve 134. The LNG then enters separator 136 with the final LNG product exiting as stream 142. In this example, no light gas 138 is evolved after the flash across valve 134, and flash gas recovery compressor 140 is not required.

Refrigeration to cool the natural gas from ambient temperature to a temperature of -102.4°C is provided by a multi-component refrigeration loop as mentioned above.

Stream 146 is the high pressure mixed refrigerant which enters heat exchanger 106 at a temperature of 32°C and a pressure of 38.6 bara. It is then cooled to a temperature of -102.4°C in heat exchangers 106 and 122, exiting as stream 148 at a pressure of 34.5 bara. Stream 148 is then divided into two portions. A smaller portion, 4.1%, is reduced in pressure adiabatically to 9.8 bara and introduced as stream 149 into heat exchanger 150 to provide supplemental refrigeration. The major portion 124 of the mixed refrigerant is also flashed adiabatically to a pressure of 9.8 bara and introduced as stream 124 into the cold end of heat exchanger 122. Stream 124 is warmed and vaporized in heat exchangers 122 and 106, finally exiting heat exchanger 106 at 29°C and 9.3 bara as stream 152. Stream 152 is then recombined with minor portion of the mixed refrigerant as stream 154 which has been vaporized and warmed to 29°C in heat exchanger 150. The combined low pressure stream 156 is then compressed in 2-stage intercooled compressor 158 to the final pressure of 34.5 bara. Liquid is formed in the intercooler of the compressor, and this liquid is recombined with the main flow 160 exiting the final compressor stage. The liquid flow is 4440 kg-mole/hr.

Thus the present invention offers an improved refrigeration process for gas liquefaction which utilizes one or more vaporizing refrigerant cycles to provide refrigeration below about -40°C and down to about -100°C , and utilizes a gas expander cycle to provide refrigeration below about -100°C . The gas expander cycle also may provide some of the refrigeration in the range of about -40°C to about -100°C . Each of these two types of refrigerant systems is utilized in an optimum temperature range which maximizes the efficiency of the particular system. Typically, a significant fraction of the total refrigeration power required to liquefy the feed gas (more than 5% and usually more than 10% of the total) can be consumed by the vaporizing refrigerant cycle or cycles. The invention can be implemented in the design of a new liquefaction plant or

can be utilized as a retrofit or expansion of an existing plant by adding gas expander refrigeration circuit to the existing plant refrigeration system.

The essential characteristics of the present invention are described completely in the foregoing disclosure. One skilled in the art can understand the invention and make
5 various modifications without departing from the basic spirit of the invention, and without deviating from the scope and equivalents of the claims which follow.

CLAIMS

1. A method for the liquefaction of a feed gas which comprises providing at least a portion of the total refrigeration required to cool and condense the feed gas by utilizing

(a) a first refrigeration system comprising at least one recirculating

5 refrigeration circuit, wherein the first refrigeration system utilizes two or more refrigerant components and provides refrigeration in a first temperature range; and

(b) a second refrigeration system which provides refrigeration in a second temperature range by work expanding a pressurized gaseous refrigerant stream.

10

2. The method of Claim 1 wherein the lowest temperature in the second temperature range is less than the lowest temperature in the first temperature range.

3. The method of Claim 1 wherein at least 5% of the total refrigeration power required to
15 liquefy the feed gas is consumed by the first refrigeration system.

4. The method of Claim 1 wherein the feed gas is natural gas.

5. The method of Claim 1 wherein the refrigerant in the first recirculating refrigeration
20 circuit comprises two or more components selected from the group consisting of nitrogen, hydrocarbons containing one or more carbon atoms, and halocarbons containing one or more carbon atoms.

6. The method of Claim 1 wherein the refrigerant in the second recirculating
25 refrigeration circuit comprises nitrogen.

7. The method of Claim 1 wherein at least a portion of the first temperature range is between about -40°C and about -100°C.

5 8. The method of Claim 7 wherein at least a portion of the first temperature range is between about -60°C and about -100°C.

9. The method of Claim 1 wherein at least a portion of the second temperature range is below about -100°C.

10

10. The method of Claim 1 wherein at least 10% of the total refrigeration power required to liquefy the feed gas is consumed by the first recirculating refrigeration system.

15

11. The method of Claim 1 wherein the first recirculating refrigeration system is operated by

- (1) compressing a first gaseous refrigerant;
- (2) cooling and at least partially condensing the resulting compressed refrigerant;
- (3) reducing the pressure of the resulting at least partially condensed compressed refrigerant;
- (4) vaporizing the resulting reduced-pressure refrigerant to provide refrigeration in the first temperature range and yield a vaporized refrigerant; and
- (5) recirculating the vaporized refrigerant to provide the first gaseous refrigerant of (1).

20

12. The method of Claim 11 wherein at least a portion of the cooling of the resulting compressed refrigerant in (2) is provided by indirect heat exchange with vaporizing reduced-pressure refrigerant in (4).

5 13. The method of Claim 11 wherein at least a portion of the cooling in (2) is provided by indirect heat exchange with one or more additional vaporizing refrigerant streams provided by a third recirculating refrigeration circuit.

10 14. The method of Claim 13 wherein the third recirculating refrigeration circuit utilizes a single component refrigerant.

15. The method of Claim 13 wherein the third recirculating refrigeration circuit utilizes a mixed refrigerant comprising two or more components.

15 16. The method of Claim 1 wherein the second recirculating refrigeration system is operated by

(1) compressing a second gaseous refrigerant to provide the pressurized gaseous refrigerant in (b);

20 (2) cooling the pressurized gaseous refrigerant to yield a cooled gaseous refrigerant;

(3) work expanding the cooled gaseous refrigerant to provide the cold refrigerant in (b);

(4) warming the cold refrigerant to provide refrigeration in the second temperature range; and

(5) recirculating the resulting warmed refrigerant to provide the second gaseous refrigerant of (1).

17. The method of Claim 16 wherein at least a portion of the cooling in (2) is provided
5 by indirect heat exchange by warming the cold refrigerant stream in (4).

18. The method of Claim 16 wherein at least a portion of the cooling in (2) is provided by indirect heat exchange with the vaporizing refrigerant of (a).

10 19. The method of Claim 16 wherein at least a portion of the cooling in (2) is provided by indirect heat exchange with one or more additional vaporizing refrigerants provided by a third recirculating refrigeration circuit.

15 20. The method of Claim 19 wherein the third recirculating refrigeration circuit utilizes a single component refrigerant.

21. The method of Claim 19 wherein the third recirculating refrigeration circuit utilizes a mixed refrigerant which comprises two or more components.

20 22. The method of Claim 1 wherein the first recirculating refrigeration circuit and the second recirculating refrigeration circuit provide in a single heat exchanger a portion of the total refrigeration required to liquefy the feed gas.

23. The method of Claim 1 wherein the first refrigerant system is operated by

(1) compressing a first gaseous refrigerant;

(2) cooling and partially condensing the resulting compressed refrigerant to yield
5 a vapor refrigerant fraction and a liquid refrigerant fraction;

(3) further cooling and reducing the pressure of the liquid refrigerant fraction, and
vaporizing the resulting liquid refrigerant fraction to provide refrigeration in the
first temperature range and yield a first vaporized refrigerant;

(4) cooling and condensing the vapor refrigerant fraction, reducing the pressure
10 of at least a portion of the resulting liquid, and vaporizing the resulting liquid
refrigerant fraction to provide additional refrigeration in the first temperature
range and yield a second vaporized refrigerant; and

(5) combining the first and second vaporized refrigerants to provide the first
gaseous refrigerant of (1).

24. The method of Claim 23 wherein vaporization of the resulting liquid in (4) is effected
at a pressure lower than the vaporization of the resulting liquid refrigerant fraction in (3),
and wherein the second vaporized refrigerant is compressed before combining with the
first vaporized refrigerant.

25. The method of Claim 16 wherein work from work expanding the cooled gaseous
refrigerant in (3) provides a portion of the work required for compressing the second
gaseous refrigerant in (1).

26. The method of Claim 16 wherein the feed gas is natural gas, the resulting liquefied natural gas stream is flashed to lower pressure to yield a light flash vapor and a final liquid product, and the light flash vapor is used to provide the second gaseous refrigerant in the second refrigerant circuit.

Accepted for filing

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ABSTRACT OF THE DISCLOSURE

5 Refrigeration process for gas liquefaction which utilizes one or more vaporizing
refrigerant cycles to provide refrigeration below about -40°C and a gas expander cycle to
provide refrigeration below about -100°C. Each of these two types of refrigerant
systems is utilized in an optimum temperature range which maximizes the efficiency of
the particular system. A significant fraction of the total refrigeration power required to
10 liquefy the feed gas (typically more than 5% and often more than 10% of the total) can
be consumed by the vaporizing refrigerant cycles. The invention can be implemented in
the design of a new liquefaction plant or can be utilized as a retrofit or expansion of an
existing plant by adding gas expander refrigeration circuit to the existing plant
refrigeration system.

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FIGURE 1

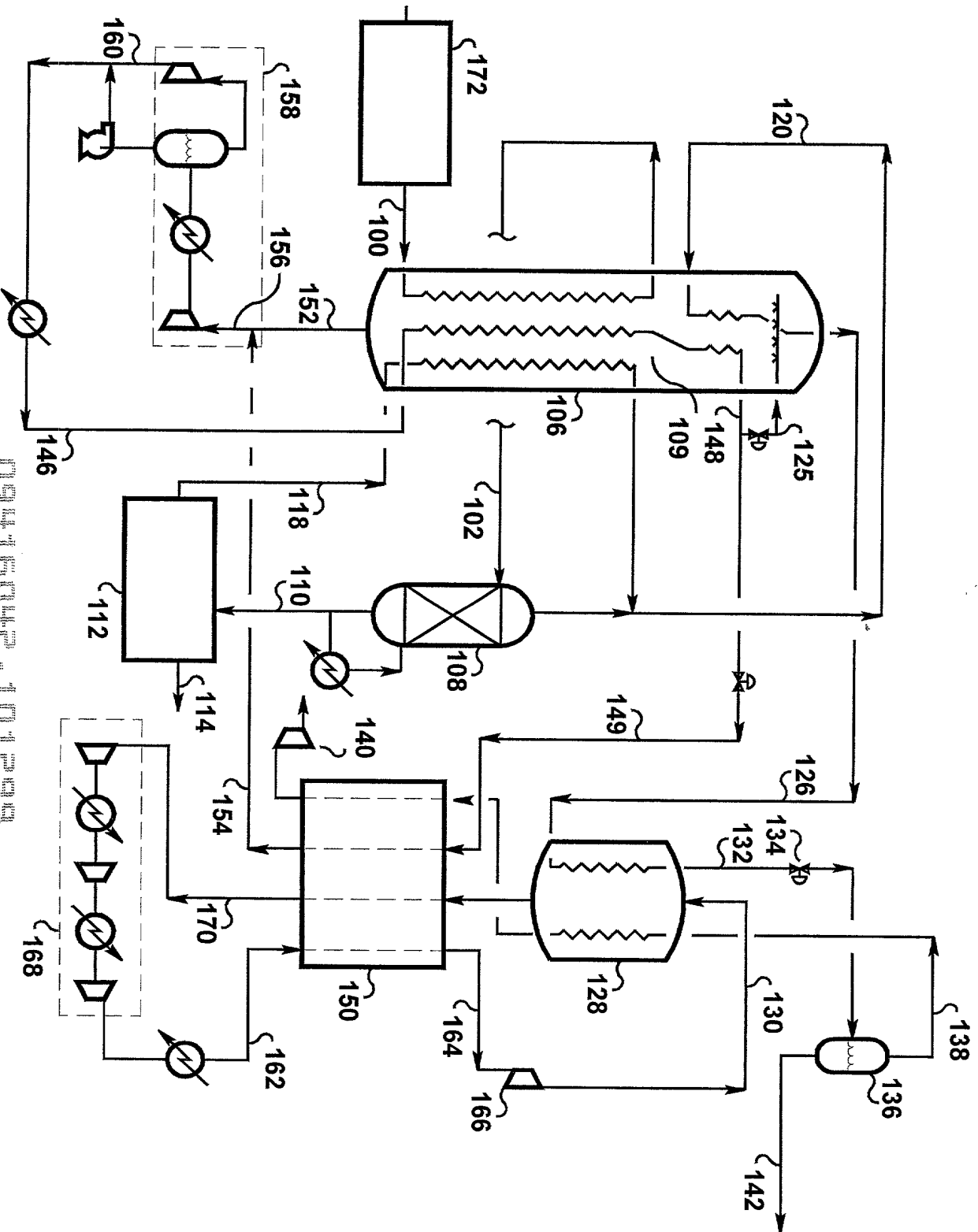


FIGURE 2

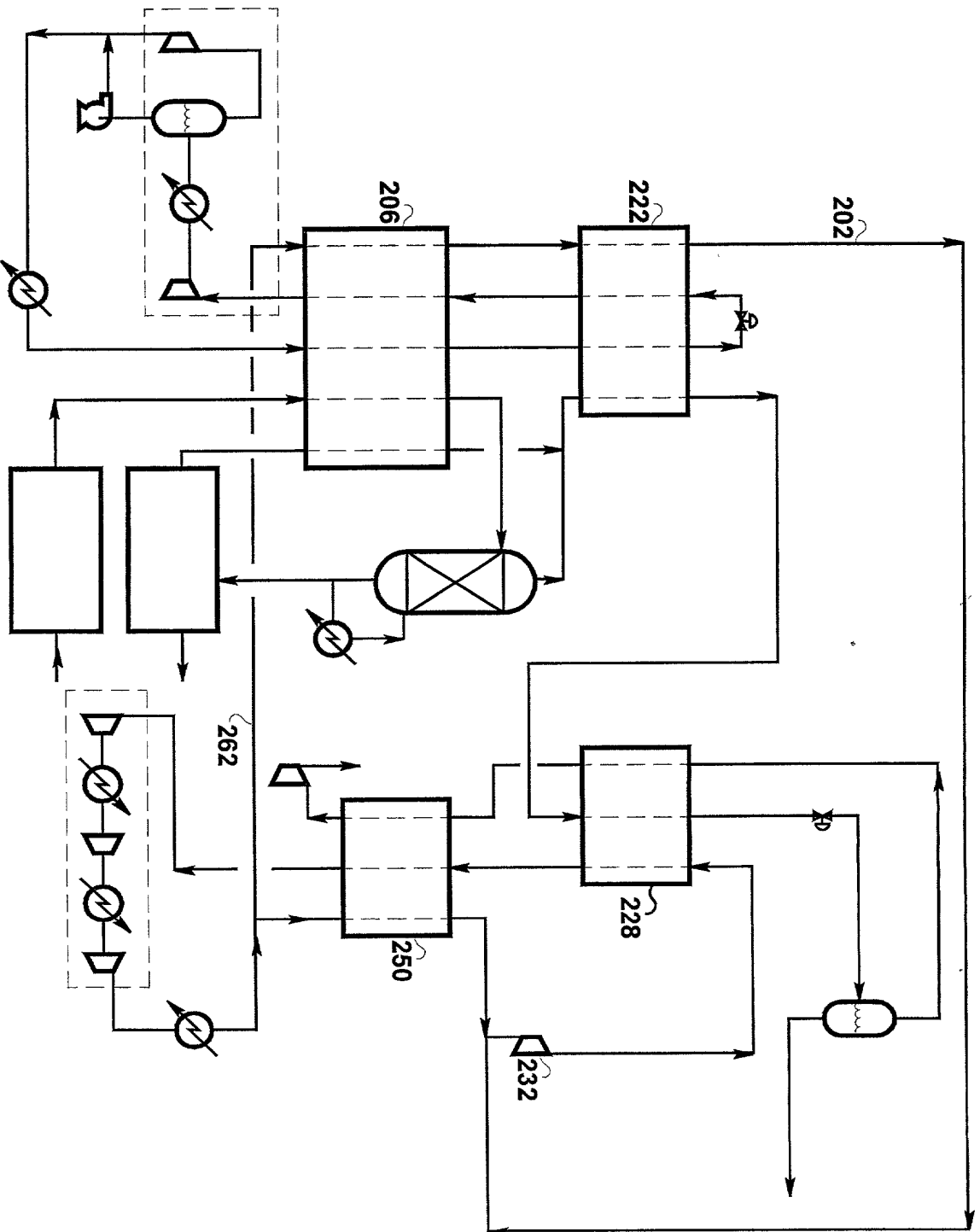


FIGURE 3

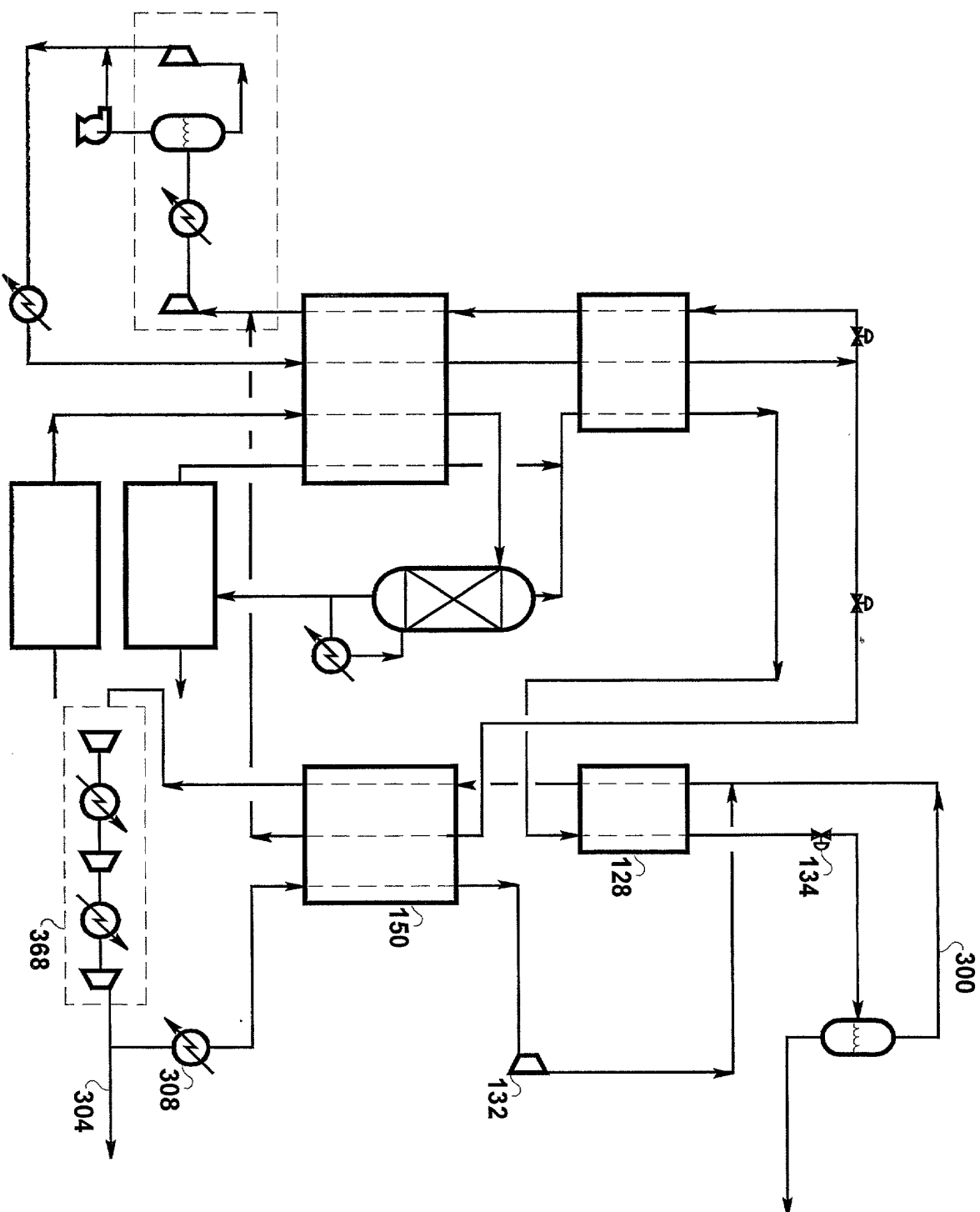


FIGURE 4

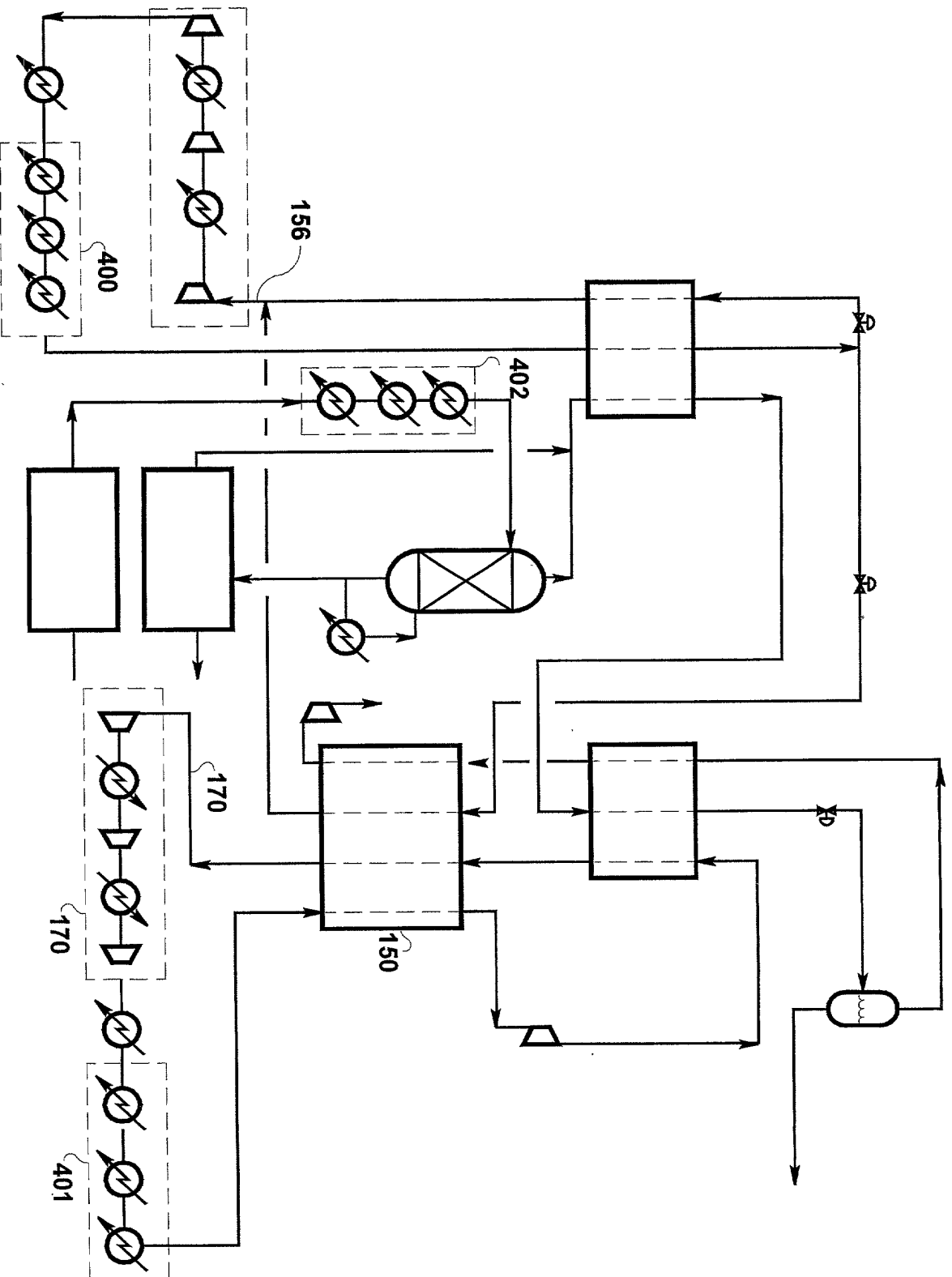


FIGURE 5

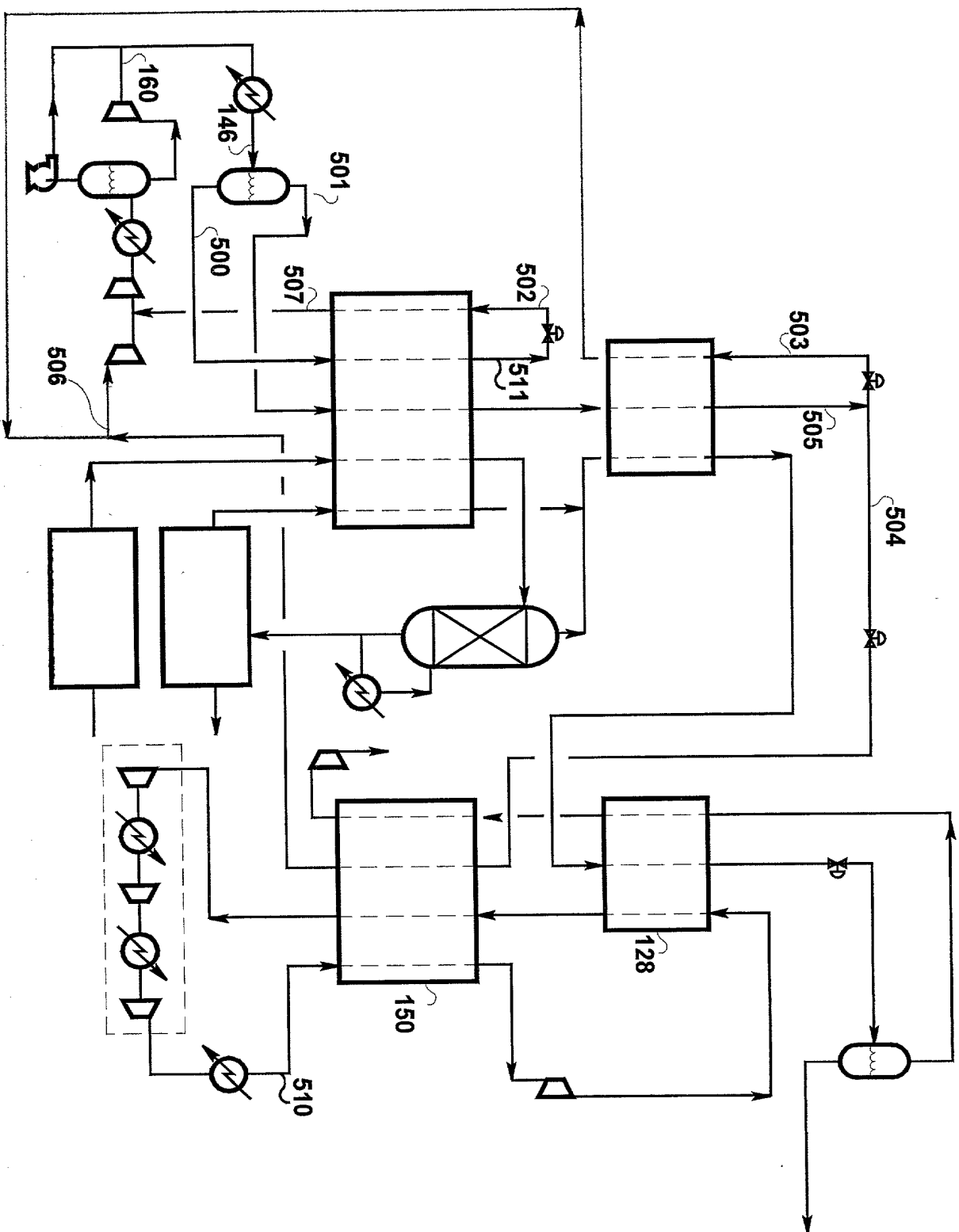


FIGURE 6

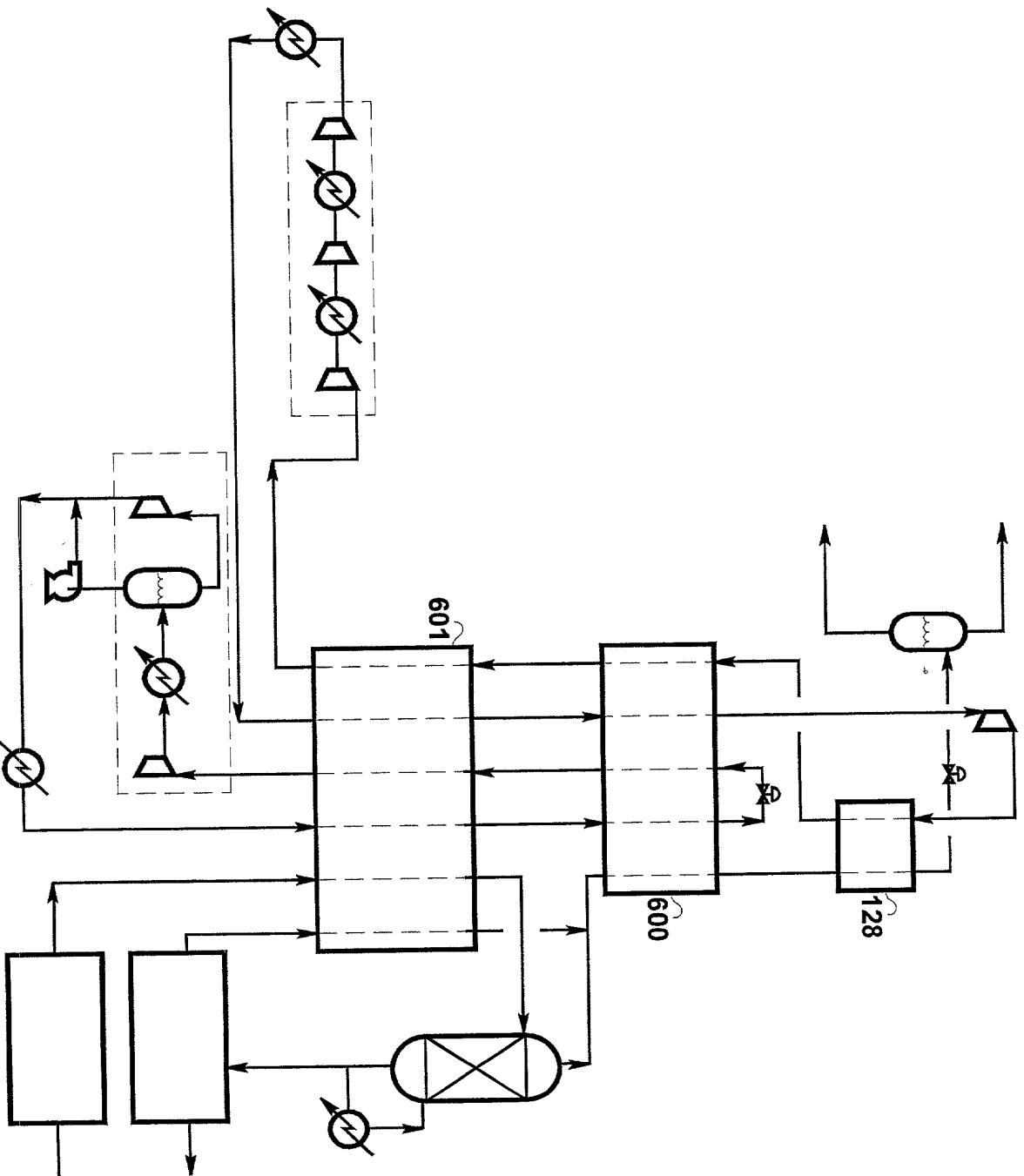


FIGURE 6

FIGURE 7

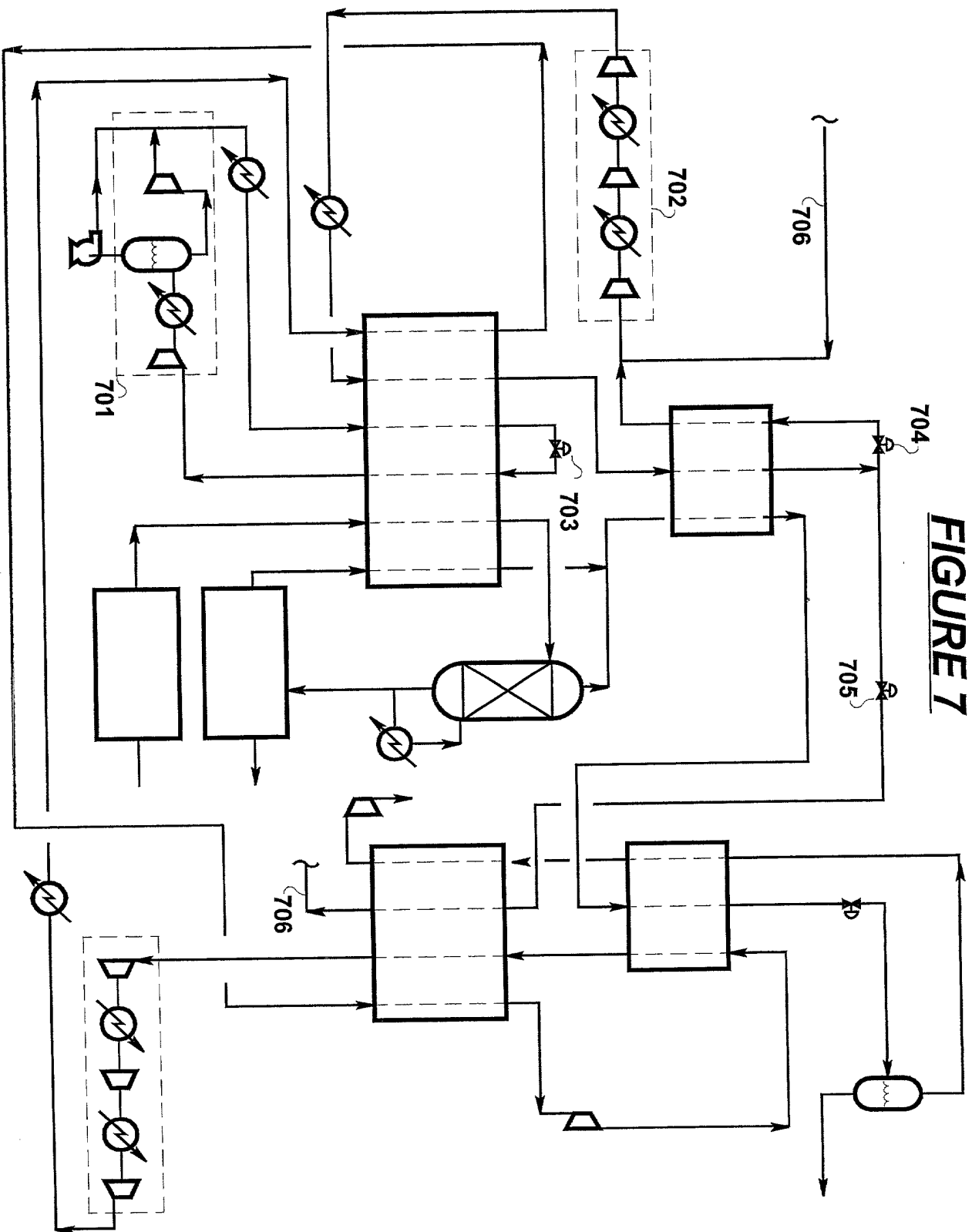


FIGURE 8

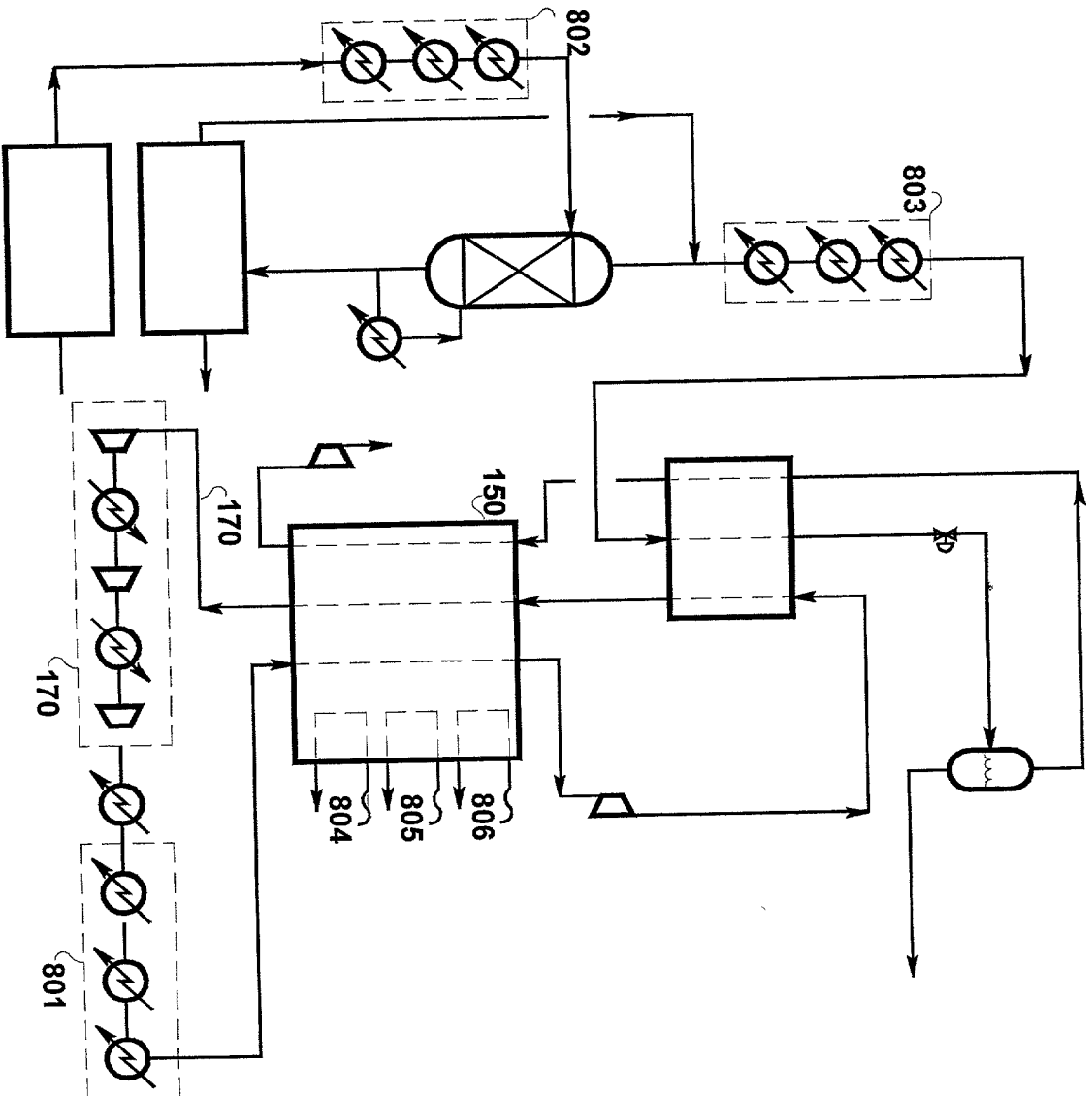
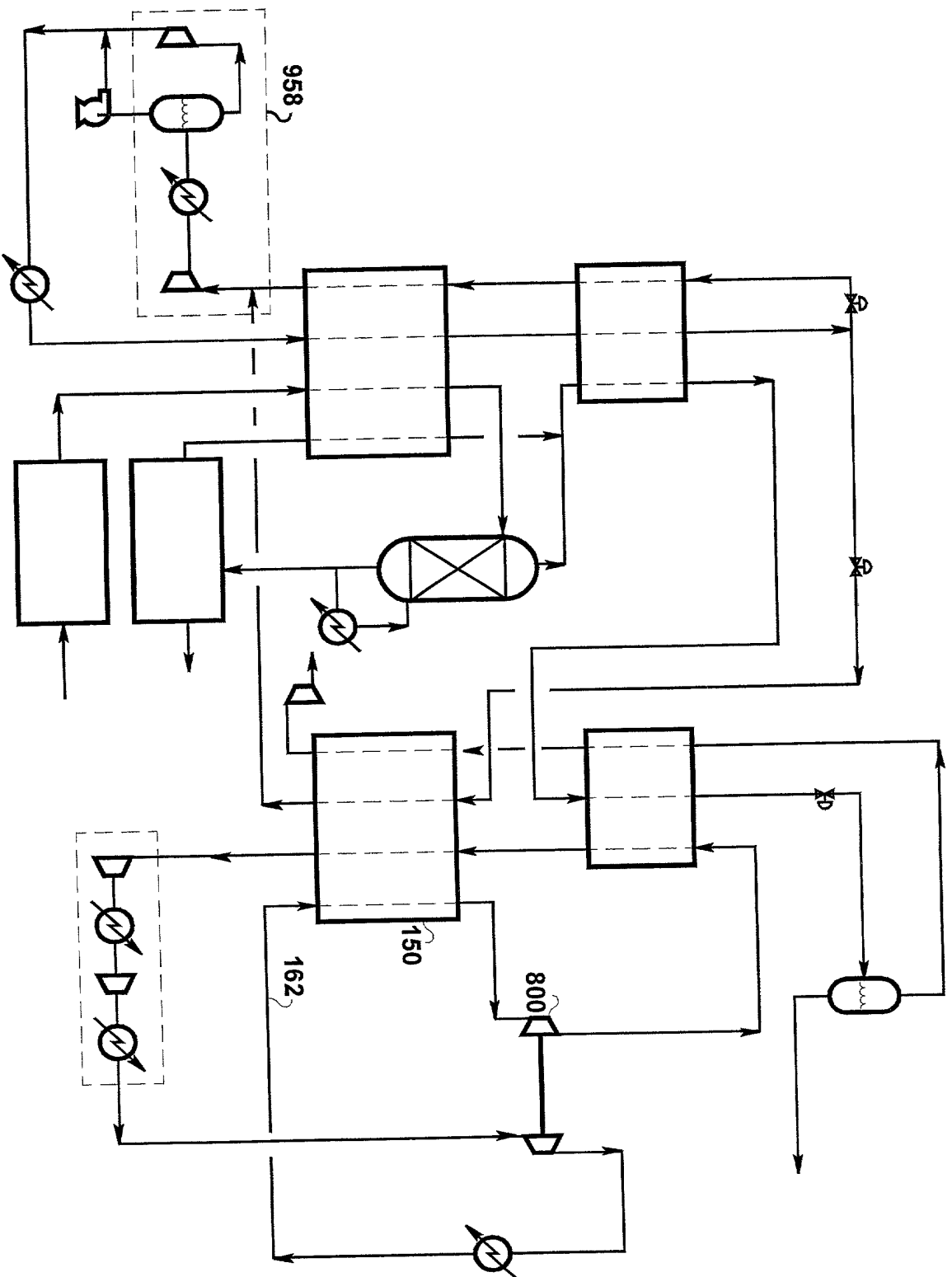


FIGURE 9



**COMBINED DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled,

HYBRID CYCLE FOR THE PRODUCTION OF LIQUEFIED NATURAL GAS

the specification of which

(check one)

☒ [X] is attached hereto.

☐ [] was filed on > as United States Application Number or PCT International Application Number > and was amended on > (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

NONE

(Number)

(Country)

(Day/month/year filed)

Priority Claimed

Y

N

[]

[]

(Number)

(Country)

(Day/month/year filed)

[]

[]

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application Serial No.) (Filing Date)

(Application Serial No.) (Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

NONE

(Application Serial No.) (Filing Date) (Status) (Patented, pending, abandoned)

(Application Serial No.) (Filing Date) (Status) (Patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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Russell L. Brewer	#25,073	Michael Leach	#27,349
Geoffrey L. Chase	#28,059	Mark L. Rodgers	#30,490
John M. Fernbacher	#32,895	Robert J. Wolff	#34,948

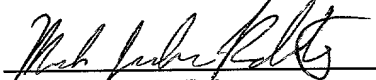
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Date: 10/12/99

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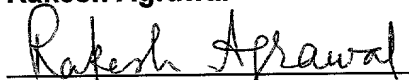
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